genation to conjugated diene was greater in helium than in air. In a related system (7) β-carotene destruction was less in oils exposed to air rather than nitrogen. This indicated a greater sensitivity to reactive intermediates, such as hydrogen atoms, than to peroxides and carbonyls, which form on irradiation in air (26).

Summary

(1) Changes in the absorption spectra of drying oils, especially safflower, on exposure to ionizing radiation were followed.
(2) Bleaching of the oil was plotted as a linear function of the logarithm of the absorption in the visible spectrum *versus* the dose.
(3) Oxygen inhibited radiation bleaching.
(4) The cost of bleaching safflower and similar oils by electrons was estimated to be about 4 cents/pound.
(5) The mechanism of radiation bleaching was postulated to involve hydrogenation of the pigments by hydrogen atoms. These were obtained by dehydrogenation of the oils or by decarboxylation of fatty acids.

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The Determination of the Unsaponifiable Matter of Tall Oil Distillates

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TALL OIL, a relatively new source of rosin and fatty acids, is derived from Southern Pine as a by-product of the kraft paper industry. Distillation of crude tall oil produces fractions which are predominately either rosin acids or fatty acids. Fatty acids of 98–99% purity are readily attainable. Impurities associated with these fatty acid fractions are rosin acids and unsaponifiable matter.

Present advances in the preparation of tall oil fatty acids are concerned with control of uniformity through chemical composition. Producers of tall oil products have therefore devoted considerable research time to perfection of analytical methods for the determination of the fatty acid, rosin acid, and unsaponifiable content of the various fractions. While procedures (2) for the determination of fatty acids and rosin acids give accurate and reproducible results, considerable controversy has arisen over determination of the unsaponifiable content of tall oil fractions.

At present two official methods are used for determining the unsaponifiable content of oils, fats, and wax products. Both require complete saponification of the sample followed by extraction of the soap solution with a suitable nonaqueous solvent. The A.S.T.M. (2) procedure specifies the use of diethyl ether as the extractant. Separatory funnels are used to separate the aqueous and nonaqueous phases. The A.O.C.S. (1) procedure recommends petroleum ether as the solvent with cylinders and glass siphons for the removal of the nonaqueous layer. A total of seven 50-ml. washes is used to remove all the water-insoluble components of the saponification mixture. The basic difference between these two methods lies in the type of solvent used for the extraction of the unsaponifiable matter.

Freyer and Weston (3) state that "the most suitable solvent to employ is probably petroleum ether fractionated to distill at 40°C. This dissolves much less soap than does methylated ether. The latter however is always safer as it dissolves a wider range of products insoluble in water." Report of the subcommittee on determination of unsaponifiable matter in oils and fats and the unsaponified fat in soaps to the standing committee on Uniformity of Analytical Methods (5) states that "there is a considerable amount of evidence that the extraction of unsaponifiable matter by means of petroleum spirit is incomplete, especially from certain fish oils."

Included in a later report on unsaponifiable matter (4) is the statement, "Attempts to use ethyl ether with the continuous and F.A.C. methods were generally unsatisfactory due to the formation of emulsions." The report also contained a comparison of per cent unsaponifiables as determined by a variety of methods using ethyl ether or petroleum ether. Results were within reasonable agreement regardless of method or solvent used.

Experimental

This paper presents data obtained in the comparison of A.O.C.S. and A.S.T.M. methods, using diethyl ether or petroleum ether for the determination of unsaponifiables in tall oil distillates. Attempts were also made to learn what factors and impurities contributed to the formation of unsaponifiable matter during processing of tall oil, fatty acid fractions.

Initial work involved investigations into effects of saponification time on yield of unsaponifiable matter. Methods require 30 to 90 min. but state that complete saponification is essential. While clarity of the solution is generally used to judge when all of the substance was saponified, it was decided to check the effects of various reflux times on actual yield of unsaponifiables.

From data of Table I it is evident that tall oil, fatty acid fractions are completely saponified in 30 min. and that increasing this time to 120 min. has no effect on the yield of unsaponifiable matter irrespective of source or unsaponifiable content. Comparison of procedures, using either ethyl ether or petroleum ether as the extractant, indicated that these solvents were equally efficient in isolating the unsaponifiable components from the aqueous soap solution. The average percentage of unsaponifiable determined with ethyl ether is slightly lower than the corresponding figures for petroleum ether. This difference does not appear significant enough to favor the use of ethyl ether over petroleum ether.

TABLE I

Comparison of Saponification Time on Yield of Unsaponifiables

Sample	Saponification time in minutes	Unsaponifiables, %
A	30	1.7, 1.6
A	90	1.4, 1.5
A	120	1.5, 1.7
A	120	1.7, 1.7
B	30	11.2, 11.2
B	90	10.8, 11.2
B	120	11.1, 11.2
C	30	10.4, 10.3
C	120	10.6, 10.7

Saponification using diethylene glycol as the solvent medium to achieve higher reaction temperature resulted in increased amounts of unsaponifiables. Extraction of the aqueous soap solution was difficult and generally resulted in emulsions which were difficult to break.

Unsaponifiable components isolated from several tall oil distillates were examined qualitatively in an effort to elucidate their composition and structure. Test for sterols by digitonin method were negative on unsaponifiables from volatile fatty acid and rosin acid fractions. Digitonin precipitation did disclose both free and combined sterols in the pitch distillation residues. Hydroxyl values were insignificantly low. Iodine value was 117. The 2,4-dinitrophenylhydrazones were obtained in good yields. These dark red crystalline derivatives melted at 145–155°C. From these data it is assumed that volatile unsaponifiable materials contained in tall oil distillates are predominantly hydrocarbons and decarboxylated fatty and rosin acid products resulting from heat degradation during distillation.

TABLE II

Comparison of Extraction Solvent on Yield of Unsaponifiables

Sample	Method	Solvent	Unsaponifiables, %
A	A.O.C.S.	Ethyl ether	1.4, 1.3
A	A.S.T.M.	Ethyl ether	1.3, 1.5
A	A.O.C.S.	Petroleum ether	1.4, 1.5
A	A.O.C.S.	Petroleum ether	1.4, 1.5
B	A.O.C.S.	Petroleum ether	10.7
B	A.O.C.S.	Ethyl ether	10.6, 10.7
B	A.O.C.S.	Ethyl ether	10.3, 10.4
C	A.O.C.S.	Ethyl ether	10.9, 11.1
C	A.O.C.S.	Petroleum ether	11.1, 11.2
D	A.O.C.S.	Petroleum ether	0.6, 0.5
D	A.O.C.S.	Petroleum ether	0.5, 0.5
D	A.S.T.M.	Ethyl ether	0.4, 0.4
E	A.S.T.M.	Ethyl ether	2.7, 3.0
E	A.O.C.S.	Petroleum ether	2.9

TABLE III

Effect of Heat Treatment [a] on Unsaponifiable Content of Fatty Acid Mixtures

Sample description	Unsaponifiables, %
Sample A	1.7, 1.7, 1.8, 1.9
Sample A + 1% abietic acid	2.0, 2.1
Sample + 5% abietic acid	3.0, 3.0
Sample + 10% tall oil rosin	2.5, 2.6
Sample + 1% sterols	2.7, 2.8
Sample + 5% Sterols	6.9, 7.0

[a] Heated for 1½ hours at 300°C. under carbon dioxide.

In an effort to learn which type of material might contribute to or act as a precursor to the unsaponifiable materials, synthetic fatty acid mixtures were made and subjected to various heat treatments. These synthetic fatty acid mixtures, containing added abietic acid, rosin, and sterols, were heated at temperatures of 300°C. From the data in Table III it would appear that abietic acid and rosin contribute to increase in unsaponifiables. Sterols apparently do not break down or contribute to increase in unsaponifiables.

Tall oil fatty acids low in rosin content show a slight increase in unsaponifiables, following heat treatment, so it would appear that heat-labile substances are contained in the tall oil rosin and presumably are the abietic acids. Further proof of this is evidenced by experiments in which methyl esters were freed of acidic rosin acids by refining with alkali. These rosin acid-free methyl esters when heated at 300°C. did not increase in unsaponifiable content, whereas the methyl esters containing original rosin acids showed an increase of about 0.4% in unsaponifiables.

TABLE IV

Effect of Heat Treatment on Unsaponifiable Content of Methyl Esters

Sample	Treatment	Unsaponifiables, %
Methyl esters, Sample A	None	1.4, 1.4
Methyl esters, Sample A	1½ hrs. at 300°C.	1.9, 1.9
Rosin acid-free, Sample A	None	1.4, 1.3
Rosin acid-free, Sample A	1½ hrs. at 300°C.	1.5, 1.5
Regenerated fatty acids [a]	None	1.3, 1.4

[a] Fatty acids regenerated from rosin acid-free methyl esters.

Summary

A comparison has been made of extraction efficiency of ethyl ether or petroleum ether in the removal of unsaponifiable matter of tall oil distillates, using the analytical procedures of A.S.T.M. or A.O.C.S. It has been shown that solvents can be used interchangeably. Results were within reasonable accuracy. Synthetic mixtures containing added abietic acid and rosin impurities, when heated at 300°C., increased in unsaponifiable content. Examination of the unsaponifiable extract from several tall oil, fatty acid fractions indicated that it was composed essentially of decarboxylated products of rosin and fatty acids.

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